# PYROLYSIS OF KEROGEN CONCENTRATE IN THE PRESENCE OF CALCIUM HYDRIDE

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Pyrolytic conversion of oil-shale kerogen to crude shale from which useful petroleum-like products can be made is an established procedure. However, the mechanism of the conversion of kerogen to shale oil, carbon residue, and gas by application of heat is not thoroughly understood. One method to study the mechanism is to pyrolyze kerogen in the presence of a hydrogen donor. The hydrogen donor should stabilize the pyrolytic products as they are formed and should provide primary thermal degradation products. Pyrolysis of kerogen in the presence of a hydrogen donor should minimize, if not eliminate, most polymerization reactions. By utilizing a system of this nature, the thermally degraded products should be more closely related to the kerogen structure and more suitable for composition study.

Pyrolytic reactions of Green River oil-shale kerogen have been studied by various investigators. McKee and Lyder (4) heated oil shale in sealed containers for 1 to 8 hours at 375°C. to 425°C., and they concluded that the kerogen degraded to a bituminous intermediate product. This intermediate product upon further heating decomposed into lower-molecular-weight oils of greater stability and higher saturation. Maier and Zimmerly (3) studied the formation of soluble bitumen by the pyrolysis of kerogen and concluded that bitumen formation was a function of temperature and time of heating. Hubbard and Robinson (2) determined the specific reaction rate for the thermal decomposition of kerogen at temperatures from 350° to 525°C. Bitumen formation increased to a maximum then dropped to zero which indicated that kerogen was converted to bitumen which on subsequent heating was cracked to gas, oil, and carbon residue. Robinson and Cummins (5) thermally extracted kerogen with tetralin, a hydrogen donor, at temperatures from 25° to 350°C. It was found that 95 percent of the kerogen was converted to a soluble product at 350°C. in 144 hours.

In studies where the compositions of thermal degradation products are correlated with the structure of kerogen, it is desirable to obtain primary degradation products that have not had an opportunity to polymerize. Polymerization does occur in unprotected thermal products as evidenced by the increase in amount of high-molecular-weight materials upon standing. Also, preliminary pyrolysis of kerogen directly into the time-of-flight mass spectrometer at this Center showed lower m/e fragment ions than are obtained from retorted shale oil. It was of interest in this study to ascertain if pyrolysis of kerogen in the presence of a hydrogen donor produced more stable products than are produced by the usual pyrolytic methods.

Pyrolysis of kerogen in the presence of calcium hydride was investigated to ascertain if pyrolysis products can be stabilized. Calcium hydride conceivably furnishes hydrogen as hydrogen radicals, hydride ions, or molecular hydrogen. Free radicals produced from kerogen could abstract a hydrogen radical from calcium hydride. Carbonium ions produced from kerogen could abstract a hydride ion from calcium hydride. Any water evolved from the kerogen concentrate as moisture, mineral water, or organic derived water could release molecular hydrogen from calcium hydride. By utilizing calcium hydride as a hydrogen donor in kerogen pyrolysis, the products should be more stable and should be more representative of initial degradation products.

This preliminary report discusses the thermal conversion of kerogen in the presence and absence of calcium hydride under both atmospheric and reduced pressures. The effect of the calcium hydride upon the pyrolysis reaction both at atmospheric and reduced pressures was determined from differences in the composition of the thermal product.

## EXPERIMENTAL

### Apparatus

The apparatus consisted of a 100 ml. round-bottom flask inverted over a gas trap (Figure 1). A heater surrounded the pyrolysis flask for sample heating. A thermocouple that extended into the flask by means of a small well controlled the temperature within the pyrolysis flask. A dry ice container which served to condense the volatile products surrounded the gas trap. The vacuum source consisted of a diffusion pump backed up by a forepump connected directly to the gas trap.

### Samples

The kerogen concentrate, prepared from Mahogany Zone oil shale of the Green River Formation from the Bureau of Mines demonstration mine near Rifle, Colorado, by a method described in a peper by Fester and Robinson, (1) contained 85 percent organic material. Benzene-soluble bitumen, mineral carbonates, and most of the quartz and feldspar were removed by this concentration method. The remaining minerals consisted of about one-half clay and other silicious minerals and one-half pyrite.

### Pyrolysis

Two grams of kerogen concentrate or mixtures of 2 grams of kerogen concentrate and 1.5 grams of calcium hydride were placed in the pyrolysis flask. Sufficient quantity of glass wool to fill the flask was added, then the sample and glass wool were agitated until the sample was dispersed uniformly in the glass wool. The apparatus was assembled, flushed out with nitrogen gas, and the cooling container was placed over the gas trap. When using reduced pressure conditions, the system was evacuated prior to heating the pyrolysis flask to the desired temperature. Runs were made at 390°C. for 20 hours. These conditions were chosen because heating kerogen for 20 hours at 390°C. gave significant conversion and permitted consecutive daily runs. All runs made at reduced pressure were at or near $10^{-4}$ Torr. Runs with calcium hydride present were made with 0.75 grams of hydride per gram of kerogen concentrate because preliminary runs were ratios of hydride to kerogen were varied suggested that this ratio provided an excess of hydride. All mixtures of kerogen concentrate and calcium hydride were ground with a mortar and pestle in a dry inert atmosphere prior to pyrolysis. The distillate material was collected in the gas trap while the soluble-pyrolytic product was extracted from the shale residue with benzene.

### Fractionation of Products

Figure 2 illustrates the method used for fractionating the pyrolysis products. The combined products were fractionated into pentane-soluble and pentane-insoluble material with pentane at 0°C. overnight. The pentane-soluble material was fractionated by elution chromatography on alumina into a predominantly hydrocarbon fraction and a polar fraction referred to as resins. In addition to these fractions, a varying amount of material was left on the columns and will be referred to as polar material not recovered. The predominantly hydrocarbon fraction was further fractionated by elution chromatography on silica gel into paraffins, aromatic oil, and polar oil. The paraffins were fractionated into normal and iso plus cycloparaffins on molecular sieves. Duplicate fractionation results checked within $\pm$ 2 percent.

## RESULTS AND DISCUSSION

The total yields based on soluble products obtained from the kerogen due to pyrolytic conversion at 390°C. for 20 hours are shown in Table 1. The yields include both the materials distilled from the kerogen concentrate and the materials made soluble but not distilled.

TABLE 1
### YIELDS OF PYROLYSIS PRODUCT

| Conditions | | Yield, weight percent of kerogen[1] |
|---|---|---|
| Pressure | CaH$_2$ | |
| Atmospheric | Yes | 59 |
| Atmospheric | No | 53 |
| Reduced | Yes | 53 |
| Reduced | No | 48 |

[1] Fischer assay equivalent 65 percent.

FIGURE 2.-Fractionation of Pyrolysis Products.



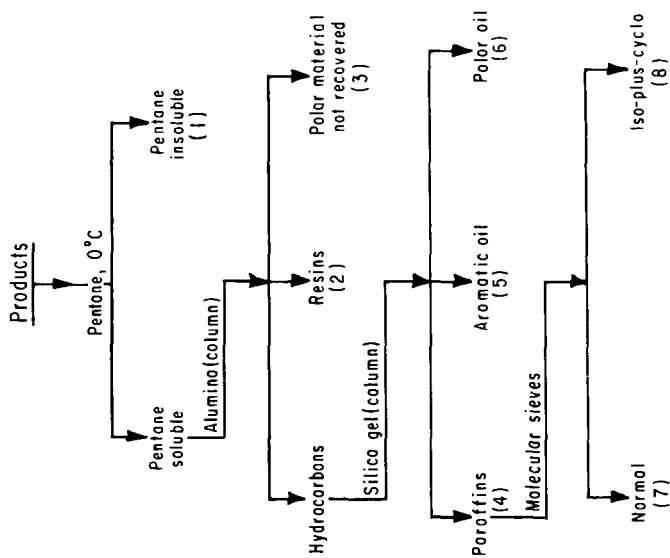FIGURE 1.-Pyrolysis Apparatus.

The amount of pyrolytic product obtained at atmospheric pressure with calcium hydride was 59 percent of the kerogen compared to 53 percent in the absence of hydride. Likewise the yield at reduced pressures with calcium hydride was 53 percent of the kerogen compared to 48 percent in the absence of hydride. At both pressure conditions, the conversion of kerogen to soluble products tended to be greatest from kerogen in the presence of calcium hydride. Reduced pressure apparently did not increase the conversion of kerogen.

The distillate and the materials made soluble but not distilled were fractionated into paraffins, aromatic oil, polar oil, resins, and pentane-insoluble material. The sum of the paraffins and aromatic oil (fraction 4 plus fraction 5), the sum of the resins and polar oil (fraction 2 plus fraction 6), the polar material not recovered from the alumina column (fraction 3), and the pentane-insoluble material (fraction 1) are shown in Table 2.

TABLE 2
YIELDS OF FRACTIONS OF THE PYROLYSIS PRODUCTS

| | Pyrolysis conditions | | | |
| | Atmospheric pressure | | Reduced pressure | |
| | With CaH$_2$ | Without CaH$_2$ | With CaH$_2$ | Without CaH$_2$ |
|---|---|---|---|---|
| Paraffins + aromatic oil (4 + 5) | 25.8 | 15.3 | 28.8 | 19.9 |
| Polar material recovered (2 + 6) | 60.4 | 45.3 | 61.7 | 55.7 |
| Polar material not recovered (3) | 8.5 | 32.4 | 7.2 | 17.8 |
| Pentane insolubles (1) | 5.3 | 7.0 | 2.3 | 6.6 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 |

The maximum amount of paraffins and aromatic oil produced under both pressure conditions was obtained from kerogen in the presence of calcium hydride. At atmospheric pressure the yield of paraffins and aromatic oil was 26 percent of the pyrolysis product when hydride was present compared to 15 percent when hydride was absent. At reduced pressures, the yield of paraffins and aromatic oil was 29 percent of the pyrolysis product when calcium hydride was present compared to 20 percent when calcium hydride was absent. This showed a substantial contribution by the calcium hydride was absent. This showed a substantial contribution by the calcium hydride to the production of more paraffins and aromatic oil. The presence of calcium hydride lowered the amount of polar material produced as shown in Table 2. The sum of the polar material recovered and the polar material not recovered at atmospheric pressure with calcium hydride, represented 69 percent of the pyrolysis product compared to 78 percent without hydride. Similarly, the total polar material, obtained at reduced pressure with calcium hydride, represented 69 percent of the pyrolysis product compared to 74 percent without hydride. Thus, with both pressure conditions smaller yields of total polar material were obtained in the presence of calcium hydride than in the absence of calcium hydride. A more significant difference in the polar material produced in the presence or absence of calcium hydride was the degree of polarity of the material produced in the presence or absence of calcium hydride was the degree of polarity of the material as evidenced by the amount of material not recovered from the alumina column. The amount of material retained on the alumina column was much less for pyrolytic products prepared in the presence of calcium hydride than in the absence of calcium hydride. At atmospheric pressure 9 percent of the product prepared in the presence of calcium hydride was retained on the alumina column compared to 32 percent of the product prepared in the absence of calcium hydride. At reduced pressure the same comparison was 7 to 18 percent. The amount of pentane-insoluble material was also less when calcium hydride was present during the pyrolysis than when calcium hydride was absent (5 percent compared to 7 percent and 2 percent compared to 7 percent).

Apparently hydrogen from the calcium hydride did combine with kerogen fragments to produce more paraffins and aromatic oil, less polar material, less highly reactive polar material, and less high-molecular-weight material in the range of pentane insolubles. Reduced pressure conditions contributed to the production of more hydrocarbons, less pentane insolubles, and less reactive polar materials than atmospheric pressure conditions.

Nuclear magnetic resonance analysis of the iso plus cycloparaffin fraction was conducted to ascertain the extent of cleavage of ring structures and functional groups. Measurement of the methyl/methylene ratio should provide information on the amount of thermal cleavage of this fraction under both pressures and in the presence or absence of calcium hydride. The iso plus cycloparaffin fraction was used for this measurement because it was essentially free of oxygen, nitrogen, and sulfur atoms and provided satisfactory spectra. The results of these determinations, shown in Table 3, suggest that reduced pressure did decrease the the methyl/methylene ratios probably because the products were removed from the pyrolysis zone before further thermal degradation could take place. The lowest methyl/methylene ratio of 0.3 was obtained for the sample heated under reduced pressure conditions in the presence of calcium hydride. No noticeable effect was found with the atmospheric pressure pyrolysis.

The results of these preliminary tests suggest that calcium hydride is a hydrogen donor in the pyrolysis reaction and tends to terminate the pyrolysis reaction by stabilizing the thermal products. Where calcium hydride was present, the pyrolysis product contained more hydrocarbons, less polar material which displayed considerably less reactivity, and less pentane-insoluble material than when calcium hydride was absent. Reduced pressure conditions contributed to the production of more hydrocarbons, less pentane-insoluble material, and less reactive polar material than did atmospheric pressure conditions. Additional work will be required to determine the exact nature of the observed differences and the significance of these differences.

TABLE 3
METHYL/METHYLENE RATIOS OF THE ISO PLUS CYCLOPARAFFIN FRACTION

| Conditions | | $CH_3/CH_2$ |
|---|---|---|
| Pressure | $CaH_2$ | |
| Atmospheric | No | 0.5 |
| Atmospheric | Yes | .5 |
| Reduced | No | .4 |
| Reduced | Yes | .3 |

ACKNOWLEDGMENT

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